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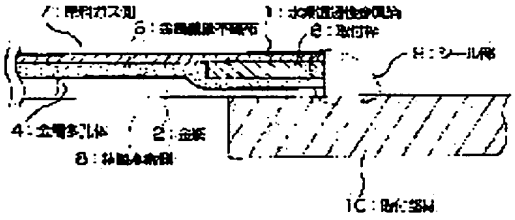
(54) HYDROGEN SEPARATION MEMBRANE

(57)Abstract:
PURPOSE: To increase yield, to enhance durability and to prevent the deterioration of hydrogen permeability by joining a mounting frame to the end edge of a metallic porous body and joining a hydrogen-permeable metallic foil to the surface of the porous body including the frame through a specified-metal layer.
CONSTITUTION: A mounting frame 6 having 0.01-1mm thickness is embedded into the end edge of the surface of a metallic porous body 4 in contact with a hydrogen-permeable metallic foil 1 so that the surface of the frame 6 is flattened and joined to the end edge. The foil 1 is joined to the surface of the porous body 4 including the frame 6 through the layer of a metal selected from Ag, Au, Pt and Cu. The yield of this hydrogen separation membrane is high in seal welding, the membrane is highly resistant to the repeated increase and decrease in temp. and pressure. Further, the hydrogen permeability of the foil is not deteriorated by the joining.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the hydrogen demarcation membrane used for a hydrogen refiner or a hydrogen manufacturing installation.
[0002]
[Description of the Prior Art] The structure of a hydrogen demarcation membrane of having the conventional hydrogen-permeability metallic foil in drawing 2 is shown. This hydrogen demarcation membrane passes the gas which contains the hydrogen of elevated-temperature high pressure in material gas side 7, and takes out hydrogen to low-pressure refining hydrogen side 8. for example, the laminated structure of the metal porous body 4 which consists of the metal-fiber nonwoven fabric 3 and/or wire gauze 2 grade for preventing breakage of the hydrogen-permeability metallic foils 1, such as an Pd-Ag alloy with a thickness of about 5-100 micrometers, and this metallic foil 1 by the pressure differential -- becoming -- **** -- attachment -- it is used, attaching in a member 10 Although each class of the metal porosity inside of the body is joined completely here, as for the metallic foil, only the periphery is joined to the metal porous body. Moreover, in order that the circumference may intercept material gas side 7, refining hydrogen side 8, and the open air, the seal of it is carried out by forming the seal section 9 by welding or packing.
[0003]
[Problem(s) to be Solved by the Invention] However, with the structure of the conventional hydrogen demarcation membrane as shown in drawing 2 , making a surrounding seal perfect has problems, like it is difficult and hydrogen-permeability ability with the yield bad as follows at the time of manufacture is low, and it is not realized industrially.
(1) Since big planar pressure cannot be applied at the time of hydrogen refining or hydrogen separation since a metallic foil's 1 being thin and the metal porous body 4 exist, therefore an operation pressure cannot be raised when carrying out a seal by packing, a big hydrogen permeation speed is not obtained.
(2) When carrying out a seal by welding, even if it uses low heat input, such as laser welding and electron beam welding, and low distorted welding, since the metallic foil 1 is thin, it melts, and it is easy to generate defects, such as omission, and the yield of a metallic foil 1 is not industrially realized at 50% or less. Although it is necessary to set thickness of a metallic foil 1 to about 0.1mm or more at least in order to raise the yield, since hydrogen permeability is in inverse proportion to the thickness of a metallic foil 1, a performance falls greatly.
[0004] this invention is made in view of the actual condition of the aforementioned conventional technology, and tends to offer the hydrogen demarcation membrane which carried out the hierarchy of the fault in the structure of the conventional hydrogen demarcation membrane.
[0005]
[Means for Solving the Problem] The hydrogen demarcation membrane which this invention makes join (1) hydrogen-permeability metallic foil to a metal porosity body surface through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu of metal layers, and is characterized by the bird clapper, (2) An attachment frame is joined to the edge section of the metal porous body to which a hydrogen-permeability metallic foil is joined so that a front face may become flat. The hydrogen demarcation membrane which is made to join a hydrogen-permeability metallic foil to the metal porosity body surface containing this attachment frame, and is characterized by the bird clapper, And an attachment frame is joined to the edge section of the metal porous body to which (3) hydrogen-permeability metallic foil is joined so that a front face may become flat. It is the hydrogen demarcation membrane which is made to join a hydrogen-permeability metallic foil to the metal porosity body surface containing this attachment frame through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu of metal layers, and is characterized by the bird clapper.
[0006] In the hydrogen demarcation membrane of this invention, what made the alloy which makes Pd or Pd a subject as a hydrogen-permeability metallic foil the thin film with a thickness of about 5-100 micrometers is used. The ternary alloy which compounded and added the aforementioned addition metal to others, Pd, Pd-Y alloy, a Pd-nickel alloy, a Pd-Cu alloy, or Pd as an example of this hydrogen-permeability metallic foil is mentioned. [alloy / Pd-Ag] Moreover, what combined the nonwoven fabric of a metal fiber, a wire gauze, or these as a metal porous body is used. As the quality of the material of this metal porous body, stainless steel, carbon steel, alloy steel, etc. can be used.
[0007] As for the front face of a metallic foil and a metal porous body, being joined is desirable, when carrying out the laminating of a hydrogen-permeability metallic foil and the metal porous body, using them and the endurance over a repeat heat cycle is taken into consideration. Although diffused junction etc. can perform junction, depending on the quality of the material of a metal porous body, an impurity is spread in a hydrogen-permeability metallic foil, and hydrogen-permeability ability may be degraded. For example, in direct junction, when the quality of the material of a

junction metal porous body is SUTERESU steel. elements, such as carbon and chromium, are spread in the metallic foil of hydrogen permeability, and hydrogen-permeability ability is reduced. Therefore, it is desirable to perform junction to a hydrogen-permeability metallic foil and a metal porous body through the metal layer of the suitable quality of the material.

[0008] The metal in which the aforementioned metal layer is made to form satisfies the following requirements.

** That to which hydrogen-permeability ability does not fall even if the component of a metal layer carries out little diffusion into a metallic foil.

** It is hard to form the good thing of junction nature, i.e., an oxide, and a recrystallizing temperature is low and junction at low temperature is possible for it.

** A thing joinable at low temperature since what has the small diffusion rate of the carbon diffused from a metal porous body and chromium, i.e., the thing in which it has a face centered cubic structure, is desirable and it makes the diffusion rate of carbon and chromium small.

[0009] Therefore, in the 1st of this invention, it is characterized by joining a hydrogen-permeability metallic foil and a metal porous body through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu of metal layers.

[0010] As a method to which it is made to join through these metal layers, the front face of a metal porous body is coated with these metals by the wet coating methods, such as the dry type coating methods, such as vacuum deposition, the sputtering method, and CVD, or electroplating, and electroless deposition, and it is common to double with a metallic foil, to overheat and pressurize and to make it join.

[0011] Moreover, in order to improve surrounding seal-weld nature, it is desirable to prepare an attachment frame in the edge section of a hydrogen demarcation membrane. Therefore, in the 2nd of this invention, in consideration of the endurance over a repeat heat cycle, as shown in drawing 1 , it is characterized by making it join to the edge section of the front face which touches the hydrogen-permeability metallic foil 1 of the metal porous body 4 in the form which embedded the attachment frame 6 with a thickness of 0.01-1mm at the metal porous body so that a front face might become flat. In addition, what is necessary is just to opt for the composition of a metal porous body suitably in consideration of the life of the high temperature strength of the material to be used, corrosion resistance, and a hydrogen demarcation membrane etc., although the metal porous body 4 is using what joined the metal-fiber nonwoven fabric 3 to the wire gauze 2 in the example of drawing 1 . the seal section according [on drawing 1 and / 7 / a refining hydrogen side and 9] to welding in a material gas side and 8, and 10 -- attachment -- it is a member

[0012] In addition, in using an attachment frame, the quality of the material uses the thing of the metal porous body to join, this quality of the material, or the approximated quality of the material. For example, when using the metal porous body made from SUS316L, it is desirable to also set the quality of the material of an attachment frame to SUS316L or nickel.

[0013] Furthermore, the 3rd of this invention has the 1st of the aforementioned this invention, and the 2nd feature.

[0014]

[Function] Only by carrying out the laminating of a hydrogen-permeability metallic foil and the metal porous body, in order that a wrinkling may arise in a metallic foil according to the difference of both coefficient of thermal expansion and distortion may concentrate there, a metallic foil is damaged in the metal fatigue by the repeat of rising and falling temperature, and leak occurs. In this invention, generating of such leak is prevented by joining a metallic foil and a metal porous body over the whole surface by meanses, such as diffused junction, beforehand. By making it join through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu as an interlayer of metal layers on the occasion of junction to a hydrogen-permeability metallic foil and a metal porous body When the quality of the material of a junction metal porous body is SUTERESU steel, in direct junction, there is an operation of being able to reduce the generating stress which elements, such as carbon and chromium, are spread in the metallic foil of hydrogen permeability, and prevents reducing hydrogen-permeability ability and which can make virtual junction temperature low and originates in a differential thermal expansion.

[0015] The yield of the hydrogen demarcation membrane at the time of carrying out the seal of the circumference by welding can be raised by joining the attachment frame for the hydrogen-permeability metallic foil to a laminating or the surface edge section which precedes carrying out a laminating and joining and touches the metallic foil of a metal porous body. In this case, only by joining an attachment frame to the front face of a metal porous body, in case a metallic foil is further joined on it, a level difference arises, local distortion (bend) is formed in a metallic foil, as a result, a metallic foil is damaged in the metal fatigue by the rising-and-falling-temperature repeat, and leak occurs. therefore, junction of the attachment frame to a metal porous body -- facing -- an attachment frame -- metal porosity -- it is required to consider as the form embedded inside of the body, and to make flat the field which joins a metallic foil

[0016] Diffused junction or soldering can perform junction in a metal porous body and an attachment frame. Moreover, before joining a metallic foil to a metal porosity body surface beforehand after junction in the method and metal porous body which attach the level difference equivalent to the thickness of an attachment frame, and an attachment frame as a method of making flat a plane of composition with a metallic foil, the method of making it flat with a press or rolling etc. can be taken.

[0017]

[Example] An example explains the hydrogen demarcation membrane of this invention still more concretely below. (Material of construction) As a hydrogen-permeability metallic foil, 20 micrometers in thickness and the 100-micrometer Pd-23%Ag rolling foil were used. Moreover, what carries out the ten-sheet laminating of the wire gauze of #40-#400 made from SUS316L to order with a fine interval, makes about 1mm in thickness, and carried out diffused junction to 6 micrometers of average apertures and the metal-fiber nonwoven fabric with a thickness of 0.1mm which consist of

SUS316L fiber as a metal porous body on condition that the temperature of 950 degrees C, welding-pressure 0.5 kgf/cm2, and Ar gas atmosphere as the wire gauze of #400 touched the metal-fiber nonwoven fabric was used. In addition, it is made to join the field of the metal-fiber nonwoven fabric of a metal porous body, and the hydrogen-permeability metallic foil used the thing made from SUS316L as an attachment frame.

[0018] (Performance evaluation) The performance evaluation of the sample produced in the following examples and the example of comparison was performed as follows.

** They are 10 kgf/cm2 at ordinary temperature. Leak examination which measures the amount of leaks from a material gas side to a refining hydrogen side by nitrogen pressure.

** They are 2 kgf/cm2 at 600 degrees C. Measurement of the hydrogen permeation speed by hydrogen gas.

** ordinary temperature -- being non-energized -- 600 degrees C and 10 kgf/cm2 the temperature and the pressure rise-and-fall examination which repeats the cycle of nitrogen pressurization, performs a leak examination for every repetition, and measures a repeat life -- operation

[0019] (Examples 1 and 2 of comparison) 20 micrometers in thickness and the 100-micrometer metallic foil made from hydrogen permeation were used, the hydrogen demarcation membrane of the structure (the conventional structure) which joins only a periphery to the front face of the aforementioned metal porous body at 900 degrees C in piles, and does not have the attachment frame of drawing 2 was produced, and the difference of seal-weld nature was investigated. With the CO2 laser welding process, the seal weld considered as 1.5kW of outputs, and speed-of-travel 50 cm/min, and supplied the SUS309 filler wire with a diameter of 0.8mm at the rate of 100 cm/min. As a result of performing the leak examination by the aforementioned ** about the obtained sample, in the example 1 of comparison whose thickness of the hydrogen-permeability metallic foil 1 is 20 micrometers, the yield of a product was 0% (the sample number / all sample numbers which were leaked are 0/3). On the other hand, although the yield of a product was 100% (3/3) in the example 2 of comparison whose thickness of a metallic foil 1 is 100 micrometers, since the thickness of a metallic foil 1 was thick, the hydrogen permeation speed by the examination of ** was small, and the performance as a hydrogen demarcation membrane was bad.

[0020] (Examples 3 and 4 of comparison) As the attachment frame 6 was welded to the circumference of the metal porous body 4 as the example 3 of comparison shows to drawing 3 , in order to use the with a thickness of 20 micrometers hydrogen-permeability metallic foil 1 and to improve seal-weld nature, and the example 4 of comparison showed to drawing 4 , the with a thickness of 0.2mm attachment frame 6 was joined to the metal porous body 4 at 950 degrees C, the laminating of the hydrogen-permeability metallic foil 1 was carried out on it, and the periphery was joined These were welded like the example 1 of comparison. As a result of performing the leak examination of ** about the obtained sample, both were 100% (2/2), and yield's were [the result of hydrogen permeation speed measurement of **] good. Then, when the temperature and the pressure rise-and-fall examination of ** were performed, leak occurred after the repetition of about 100 - 200 times. Except the time of a periodic check, with the equipment which continues steady operation, although a life of this level is enough, the equipment which repeats starting of every day and every week equipment and a halt requires a further long-term repeat life.

[0021] (Example 5 of comparison) When the sample which examined in the examples 3 and 4 of comparison was cut and the cross section was investigated, as shown in drawing 3 and drawing 4 , it turns out that leak has occurred from the attachment frame 6, the level difference section P of the weld zone of the metal porous body 4 or the attachment frame 6, and the portion into which the metallic foil 1 bent in the level difference section Q of the metal porous body 4. Then, it is the sample which carried out like the example 4 of comparison, and was obtained all over a diffused-junction furnace The temperature of 1050 degrees C, and 1 kgf/cm2 It was made for the field which heats, pressurizes by the pressure, pushes in the attachment frame 6 into the metal porous body 4, and touches a metallic foil 1 to become flat. Consequently, about 800 times of repeats were able to be borne by the temperature and the pressure rise-and-fall examination of **. In addition, rolling can also perform surface flattening.

[0022] (Example 6 of comparison) When repeating starting of equipment, and a halt every day, it is required to bear in three years and to bear 1825 times of repeats in five years 1095 times. If the sample after performing the temperature and a pressure rise-and-fall examination of ** in the example 5 of comparison is investigated, the wrinkling will be formed in the Pd-Ag foil, and it was thought that **** resulting from the coefficient-of-thermal-expansion difference of an Pd-Ag foil and a metal porous body concentrated on this portion. Then, in order to prevent formation of a wrinkling, the whole surface surface of the metal porous body 4 was joined to the Pd-Ag foil 1 by diffused junction. Junction conditions carried out vacuum length of the diffused-junction furnace, and pressurized it at 900 degrees C. Although it came to bear about 2000 times of repeats by the temperature and a pressure rise-and-fall examination of **, in spite of having used 20 micrometers in thickness, and the thin Pd-Ag foil by this, hydrogen permeation speed was small. When component analysis of the cross section of this Pd-Ag foil was performed, it turns out that carbon and chromium are spread in an Pd-Ag foil from the metal porous body, and this is degrading the hydrogen-permeability ability of an Pd-Ag foil.

[0023] (Examples 1-5) The hydrogen-permeability metallic foil 1 and the metal porous body 4 which joined the attachment frame with a thickness of 0.2mm and carried out flattening of the front face were completely joined through the layer of Ag, Au, nickel, Pt, or Cu, and the hydrogen demarcation membrane of the structure shown in drawing 1 was produced. Vacuum deposition performed the formation method of a metal layer. The obtained sample of a hydrogen permeation speed according [all] to hydrogen permeation speed measurement of ** was good, and generating of leak of even 2500 times or more of repeats of the result of the temperature and a pressure rise-and-fall examination of ** was accepted. The test result of the sample of the examples 1-6 of comparison and examples 1-5 is collectively shown in Table 1.

[0024]

[Table 1]

比較例 実施例	番号	試作条件						性能評価結果					総合評価
		Pd-Ag 箔厚さ (μm)	取付枠の有無	取付枠埋込み(平坦化)の有無	Pd-Ag 箔と金属多孔体の接合有無	中間層の種類	接合温度 (℃)	①常温リーク試験 10kgf/cm^2	③ 温度・圧力昇降試験			②水素透過速度 (※1)	
									100 回以上	365 回以上	1825回以上		
比較例	1	20	無	無	無	−	900	×	−	−	−	−	×
	2	100	無	無	無	−	900	○	−	−	−	△ (50)	△
	3	20	有 (溶接)	無	無	−	900	○	○(116) (195)	−	−	○ (220)	○
	4	20	有 (挿入)	無	無	−	900	○	○(144) (178)	−	−	○ (220)	○
	5	20	有 (挿入)	有	無	−	900	○	○	○(799)	−	○ (220)	○
	6	20	有 (挿入)	有	有	−	900	○	○	○	○(1940)	△ (160)	△
実施例	1	20	有 (挿入)	有	有	Ag	550	○	○	○	○(2000<)	○ (220)	◎
	2	20	有 (挿入)	有	有	Au	550	○	○	○	○(2000<)	○ (220)	◎
	3	20	有 (挿入)	有	有	Ni	900	○	○	○	○(2000<)	○ (220)	◎
	4	20	有 (挿入)	有	有	Pt	900	○	○	○	○(2000<)	○ (220)	◎
	5	20	有 (挿入)	有	有	Cu	900	○	○	○	○(2000<)	○ (220)	◎

※1 水素透過速度の単位： $cm^3/cm^2 \cdot min \cdot atm^{0.5}$

[0025]
[Effect of the Invention] The hydrogen demarcation membrane of this invention has a large yield in the case of a seal weld, and its endurance over the rise-and-fall repeat of temperature and a pressure is high. Furthermore, in what was joined through the metal layer between the hydrogen-permeability metallic foil and the metal porous body, degradation of the hydrogen-permeability ability of the metallic foil by junction can be prevented.

[Translation done.]

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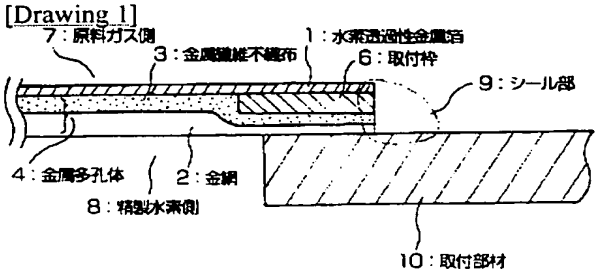
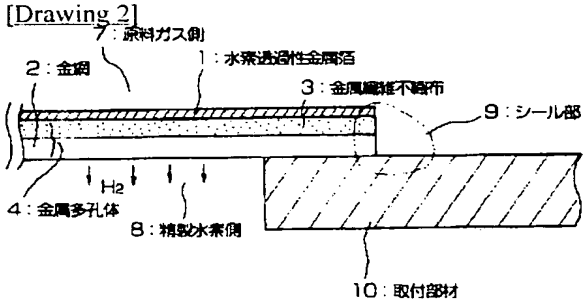
DRAWINGS

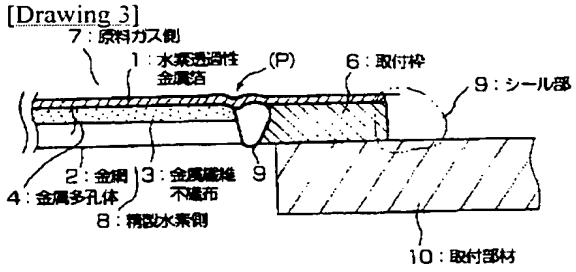
[Drawing 1]



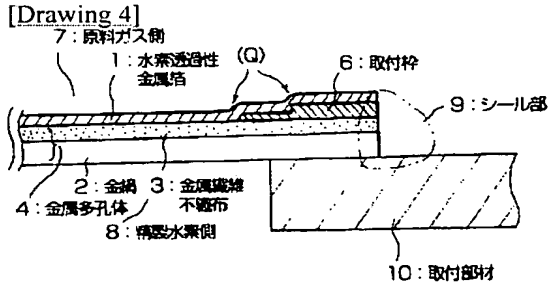
[Drawing 2]



[Drawing 3]



[Drawing 4]



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CLAIMS

[Claim(s)]
[Claim 1] The hydrogen demarcation membrane which is made to join a hydrogen-permeability metallic foil to a metal porosity body surface through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu of metal layers, and is characterized by the bird clapper.
[Claim 2] The hydrogen demarcation membrane which joins an attachment frame to the edge section of the metal porous body to which a hydrogen-permeability metallic foil is joined so that a front face may become flat, is made to join a hydrogen-permeability metallic foil to the metal porosity body surface containing this attachment frame, and is characterized by the bird clapper.
[Claim 3] The hydrogen demarcation membrane which joins an attachment frame to the edge section of the metal porous body to which a hydrogen-permeability metallic foil is joined so that a front face may become flat, is made to join a hydrogen-permeability metallic foil to the metal porosity body surface containing this attachment frame through one which is chosen from the group which consists of Ag, Au, Pt, nickel, and Cu of metal layers, and is characterized by the bird clapper.

[Translation done.]